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A Simple Way for Obtaining the Expression for the Entropy of Fluid

III. The Mean Spherical Approximation

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Abstract

The more simple technique is used to obtain the analytical expression of the entropy for the square-well fluid in the mean spherical approximation.

Keywords: Entropy, square-well fluid, mean spherical approximation

In the previous article (I) was shown a more simple way to obtain the entropy, S, of an equilibrium arbitrary fluid with the hard-core (HC) pair potential.

Here, we apply this way to the square-well (SW) model within the mean spherical approximation (MSA) [1].

The SW pair potential is

$$\varphi_{\mathrm{SW}}(r)=\begin{cases}\infty, & r<\sigma \\ \varepsilon, & \sigma\le r<\lambda\sigma \\ 0, & r\ge\lambda\sigma\end{cases}, \tag{1}$$

where ε, λ and σ are the SW parameters.

The Fourier transform of the attractive part of $\varphi_{\mathrm{SW}}(r)$ is

$$\phi_{\mathrm{SW}}(q)=\frac{4\pi\varepsilon}{q^3}[\sin(q\lambda\sigma)-\sin(q\sigma)-q\lambda\sigma\cos(q\lambda\sigma)+q\sigma\cos(q\sigma)] \quad . \tag{2}$$

The expression for the Fourier transform of the direct correlation function, $c(r)$, in the SW-MSA approach we represent as

$$c_{\mathrm{SW\text{-}MSA}}(q)=c_{\mathrm{SA}}(q)-\beta\phi_{\mathrm{SW}}(q), \tag{3}$$

where $\beta=(k_{\mathrm{B}}T)^{-1}$, T is the absolute temperature, k_{B} - Boltzmann constant, $c_{\mathrm{SA}}(q)$ - the semi-analitical (SA) expression obtained in [2]:

$$c_{\mathrm{SA}}(q)=\left(\frac{4\pi}{q^3}\right)\left\{\sum_{m=1}^{n+2}x^{2-m}\frac{\partial^m\sin(x)}{\partial x^m}\sum_{l=0}^{n}b_l\prod_{k=0}^{m-2}(l+1-k)+\sum_{m=1}^{(n+1)/2}\frac{(-1)^{m+1}(2m)!b_{2m-1}}{x^{2m-1}}\right\} \tag{4}$$

Here, the coefficients b_m are calculated numerically from the condition, that the radial distribution function is equal to zero inside the HC; $x=q\sigma$.

The structure factor, $a(q)$, of the SW system within the MSA(SA) is written as

$$a_{\mathrm{SW\text{-}MSA(SA)}}(q)=\frac{1}{1-\rho c_{\mathrm{SA}}(q)+\beta\rho\phi_{\mathrm{SW}}(q)} \quad . \tag{5}$$

Finally, using Eq.(10) from (I) we have the following expression for the entropy:

$$S_{\mathrm{SW\text{-}MSA(SA)}}=S_{\mathrm{HS}}+\frac{k_{\mathrm{B}}}{4\pi^2}\int_0^{\infty}dqq^2\left(\beta a_{\mathrm{SW\text{-}MSA(SA)}}(q)\phi_{\mathrm{SW}}(q)+\frac{1}{\rho}\ln\frac{a_{\mathrm{SW\text{-}MSA(SA)}}(q)}{a_{\mathrm{HS}}(q)}\right). \tag{6}$$

Here, $a_{\mathrm{HS}}(q)$ is the hard-sphere (HS) $a(q)$, taken in the analytical form [3], ρ - mean atomic density. Eq.(6) can be transformed exactly to Eq.(13) obtained in [4].

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